Supporting Information

Enhancing Propylene/Propane Separation Performances of

ZIF-8 Membranes by Post-Synthetic Surface Polymerization

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Figure S1. SEM images of a ZIF-8 seed layer: **a** top view and **b** cross-sectional view.



Figure S2. a ¹H NMR spectra of his-BiB, ZIF-8, and ZIF-8-BiB membranes and **b** his-BiB contents of ZIF-8-BiB membranes as a function of different PSLE reaction times. The unidentified signals in (a) are attributed to TEA·HBr salt as a byproduct.



Figure S3. SEM images of ZIF-8-BiB membranes treated for different PSLE times: **a** 12 h , **b** 24 h, **c** 36 h, and **d** 48 h.



Figure S4. Diffraction patterns of ZIF-8-BIB membranes for different PSLE times.



Figure S5. PXRD patterns of a ZIF-8 membrane, a ZIF-8-BiB membrane, and a ZIF-8-PMMA membrane.



Figure S6. FT-IR spectra of his-BiB, bulk PMMA, ZIF-8 membrane, ZIF-8-BiB membrane, and ZIF-8-PMMA membrane.



Figure S7. ¹H NMR spectrum of PMMA obtained from a digested ZIF-8-PMMA membrane.



Figure S8. Thermograms of ZIF-8, ZIF-8-BiB, and ZIF-8-PMMA membranes. Note that the weight of the α -Al₂O₃ substrate was subtracted.



Figure S9. EDX elemental mapping images of a ZIF-8-PMMA membrane.



Figure S10. Cu 2p3/2 XPS spectra and deconvoluted curves of a ZIF-8-PMMA membrane.

| Sample | No. | C ₃ H ₆ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹) | C ₃ H ₈ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹) | C ₃ H ₆ /C ₃ H ₈ separation factor |
|------------|------|--|--|---|
| ZIF-8 | 1 | 4.04 x 10 ⁻⁸ | 4.57 x 10 ⁻¹⁰ | 88.5 |
| | 2 | 3.76 x 10 ⁻⁸ | 6.31 x 10 ⁻¹⁰ | 59.6 |
| | 3 | 4.47 x 10 ⁻⁸ | 10.6 x 10 ⁻¹⁰ | 42.1 |
| | Ave. | $4.31 \pm 0.53 \text{ x } 10^{-8}$ | $7.17 \pm 2.54 \text{ x } 10^{-10}$ | 60.1 ± 13.9 |
| ZIF-8-BiB | 1 | 3.35 x 10 ⁻⁸ | 5.80 x 10 ⁻¹⁰ | 57.8 |
| | 2 | 3.33 x 10 ⁻⁸ | 7.53 x 10 ⁻¹⁰ | 44.3 |
| | 3 | 3.07 x 10 ⁻⁸ | 8.66 x 10 ⁻¹⁰ | 42.1 |
| | Ave. | $3.25 \pm 1.57 \text{ x } 10^{-8}$ | $7.33 \pm 1.44 \ge 10^{-10}$ | 44.4 ± 6.6 |
| ZIF-8-PMMA | 1 | 4.23 x 10 ⁻⁸ | 3.97 x 10 ⁻¹⁰ | 106.6 |
| | 2 | 7.82 x 10 ⁻⁸ | 7.42 x 10 ⁻¹⁰ | 105.3 |
| | 3 | 4.68 x 10 ⁻⁸ | 4.47 x 10 ⁻¹⁰ | 104.7 |
| | Ave. | $5.58 \pm 1.82 \ge 10^{-8}$ | $5.29 \pm 1.86 \text{ x } 10^{-10}$ | 105.5 ± 2.8 |

Table S1. Permeation data measured at room temperature and ~ 1 atm.

| Sample | MMA (mmol) | ZI | F-8 | ZIF-8-PMMA | |
|------------|---------------|--|---|--|---|
| | | C ₃ H ₆ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹) | C ₃ H ₆ /C ₃ H ₈ separation factor | C ₃ H ₆ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹) | C ₃ H ₆ /C ₃ H ₈ separation factor |
| S1 | 0.14 | 6.39 x 10 ⁻⁸ | 4.2 | 5.35 x 10 ⁻⁸ | 6.1 |
| S2 | 0.14 | 3.79 x 10 ⁻⁸ | 21.0 | 4.33 x 10 ⁻⁸ | 54.3 |
| S3 | 0.14 | 4.38 x 10 ⁻⁸ | 61.3 | 5.57 x 10 ⁻⁸ | 105.6 |
| S4 | 0.28 | 4.74 x 10 ⁻⁸ | 58.1 | 2.94 x 10 ⁻⁸ | 108.8 |
| S5 | 0.69 | 5.62 x 10 ⁻⁸ | 3.2 | 1.79 x 10 ⁻⁸ | 59.6 |
| S 6 | 0.69 | 4.17 x 10 ⁻⁸ | 9.8 | 1.47 x 10 ⁻⁸ | 90.9 |
| S7 | 0.69 | 4.46 x 10 ⁻⁸ | 66.0 | 1.20 x 10 ⁻⁸ | 100.5 |

 Table S2. Permeation results of ZIF-8 membranes and the corresponding ZIF-8-PMMA membranes.



Figure S11. SEM images of ZIF-8-PMMA membranes with different PMMA thicknesses controlled by the contents of MMA during the ATRP step. The MMA content varies from 0.1 mmol (**a**, **b**), to 0.3 mmol (**c**, **d**), and to 0.7 mmol (**e**, **f**). On the left are the top views and on the right the cross-sectional views.



Figure S12. Long-term C_3H_6/C_3H_8 separation performance of the ZIF-8-PMMA membrane.